Size Induced Glass Transition in Ultra-Thin Films and Its Impact in Diffusive and Elastic Behavior

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It has been experimentally observed that the glass transition temperature of ultra thin free-standing polymeric films decreases with respect to the bulk value of the material. This trend, however, appears to be reversed in the presence of strongly attractive substrates. We have performed ellipsometry, local probe calorimetry, and molecular simulations to measure the glass transition temperature of ultra thin films. The results of ellipsometry and calorimetry measurements are fully consistent. The findings of our simulations provide useful insights into the observed experimental behavior. These findings indicate that two distinct regions are formed in the thin films: a low mobility region near a strongly attractive substrate, and a high mobility region near a free surface. While high mobility is consistent with a lower glass transition temperature, low mobility tends to increase it. In order to better understand the mechanisms behind glass transition changes at small length scales, self-diffusion coefficients were also determined in the bulk, and in supported and free-standing films. The results of these calculations are also consistent with experimental data.

The apparent changes of glass transition temperature in ultra thin films could have serious implications for nanolithography. In order to explore the types of changes that can be expected in the mechanical properties (e.g. elastic constants) of nano scale structures, we have also performed a series of simulations of structure deformation. The results of these calculations indicate that the Young's modulus of a polymeric material can undergo tremendous changes when the size of a structure is in the sub-100 nanometer range. It is shown that the aspect ratio of the feature, the temperature of the system, and the characteristics of the surface all influence strongly the elastic behavior of very small structures.